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Physics Procedia 55 (2014) 324 – 328

Physics Procedia

Eighth International Conference on Material Sciences (CSM8-IMS5)

First-principles study of high-pressure phases of AlN

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Abstract

We report study of high-pressure phases of AlN compound, using a recent version of the full potential linear muffin-tin orbitals method (FPLMTO) which enables an accurate treatment of the interstitial regions. The Exchange-correlation has been accounted for within LDA using the exchange-correlation potential calculated by Perdew et al. Calculations are given for lattice parameters, bulk modulus and its first derivatives in the wurtzite, zinc-blende, rock-salt, CsCl, NiAs, βSn, the Cinnabar and the hexagonal structures. The results of these calculations are compared with the available theoretical and experimental data.

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Keywords: AlN; PLW-FPLMTO method; Pressure; Phase transition;

1. Introduction

Among the III-V nitride compounds, aluminum nitride (AlN) is one of the most interesting materials, operating under extreme conditions. In the bulk form, AlN stabilizes in the wurtzite phase at ambient conditions. However, it is known that AlN can be grown in zinc-blende phase under appropriate conditions [1,2-3]. When pressure is applied, materials often exhibit new crystal phases and novel behavior. Under high pressure, AlN and other nitrides go through a phase transition from the wurtzite to the rocksalt lattice structure [4,5].

Experimental research and theoretical studies on the physical properties of group-III nitrides at high pressure has seen much activity in recent decades, however, there is still a lack of knowledge of such properties that will only be gained by a consensus of a number of independent studies In an attempt to help understand the bulk structural parameters of AlN in different phases, and to gain more information about the transition sequence we report a detailed calculation of structural properties of AlN in the wurtzite(B4), zinc-blende (B3), rock-salt (B1), CsCl (B2), NiAs($B8_1$), βSn (A5), the Cinnabar (B9) and the hexagonal(hex) [6] structures at zero temperature. When the

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Peer-review under responsibility of the Organizing Committee of CSM8-ISM5
doi:10.1016/j.phpro.2014.07.047

internal parameter u of the wurtzite structure takes the value ½, the symmetry changes to space group $P6m_2$. In this case the calculated optimal value of the axial ratio for this structure refers to as hexagonal(hex) one [7], is c/a =1.23. The paper is organized as follows. The method is briefly commented in Section 2. Results are discussed in Section 3, and then conclusions are summarized in Section 4.

2. Theoretical Framework

At the reverse of the previous LMTO methods, the present FPLMTO treats the interstitial regions on the same footing with the core regions. The non-overlapping muffin tin spheres potential is expanded in spherical harmonics inside the spheres and Fourier transformed in the interstitial regions [8]**.** The exchange-correlation has been accounted for within LDA using the exchange-correlation potential calculated by Perdew et al. The available computer code lmtART [8,9] was used in the present work.

The LDA approximation has turned out to be much more successful than originally expected [10], in spite of its extreme simplicity, the LDA accurately describes structural and lattice dynamical properties for materials such as semiconductors, the correct structure is usually found to have the lowest energy, while bond lengths and bulk moduli are accurate to within a few percent [6].

The details of calculations are the following. Both LMTO-basis set and charge density is expanded inside the muffin-tin spheres in spherical harmonic functions with cut-off l_{max}, and in Fourier series in the interstitial region. In the muffin-tin spheres (MTS) of radius RMT, the upper limit on the angular momentum expansion of the smoothed Hankel functions about a given atomic site is carried out up to l_{max}=6. In the interstitial region, the s, p and d basis functions are expanded in a number (NPLW) of plane waves determined automatically by the cut-off energies. In order to achieve convergence of energy eigenvalues, the wave functions in the interstitial region is expanded in plane waves with a cutoff of R_{MT} x K_{MAX} equal to 8 where K_{MAX} is the maximum modulus for the reciprocal lattice vector, and R_{MT} is the average radius of the MT spheres.

3. Results and discussion

3.1. Structural properties

Using the present FPLMTO for the binary compounds AlN, we have calculated the equilibrium volume corresponding to the lowest total energy, the equilibrium lattice constants (*a*, *b* and *c* in the X, Y and Z directions, respectively), the bulk modulus and its derivative by fitting the total energy as a function of volume to the Murnaghan equation of state [11].

The structural optimization was performed for the variables *u*, *c*/*a* and *V* in the wurtzite(B4), hexagonal(hex), and NiAs($B8_1$) phases. For *u, v*, *c*/*a* and *V* in Cinnabar (B9) phase, and for the two variables *c*/*a* and *V* in the βSn (A5) phase, *u* and *v* being the internal parameters and *V* the volume. For all the other phases this operation was performed for the volume *V* only. The electronic configurations used in the present calculations are: $3s^2\ 3p^1$ for Al and $2s^2\ 2p^3$ for N.

The total energy variations with volume for the different phases are displayed in Fig. 1. Volume and energy are per single formula unit. In this graph the wurtzite and NiAs structures are optimized in the sense that the internal parameter c/a and u have varied until the energy is minimal. However, the determination of the optimal c/a and u was simpler for $B8_1$ than B4 phase because the value of u in the case of the NiAs phase tends to keep its ideal value equal to 0.25. We have also optimized the cinnabar structure which, upon relaxation, has internal parameters $u = v =$ 0.5. Whereas this is not the case for the βSn structure .For this later, we keep the value of c/a = 0.5264 as Ref.12.

Our calculations show in Fig.1, that the ground state configuration for AlN is the wurtzite (B4) structure at ambient conditions. Nevertheless, depending on the pressure, AlN compounds exhibit hexagonal, NaCl and NiAs phases from wurtzite or ZB structures.

The curves of Fig.1 are fit to Murnaghan's equation of state in order to determine the equilibrium structural parameters. Where our results are summarized and compared with some available experimental data and recent published calculations given in Table1.

We notice for wurtzite, zinc-blende and rock-salt structures, a good agreement with literature. In particular, for wurtzite (B4) structure the lattice constants used in our calculation are so closed to Ref.13 and Ref.14.

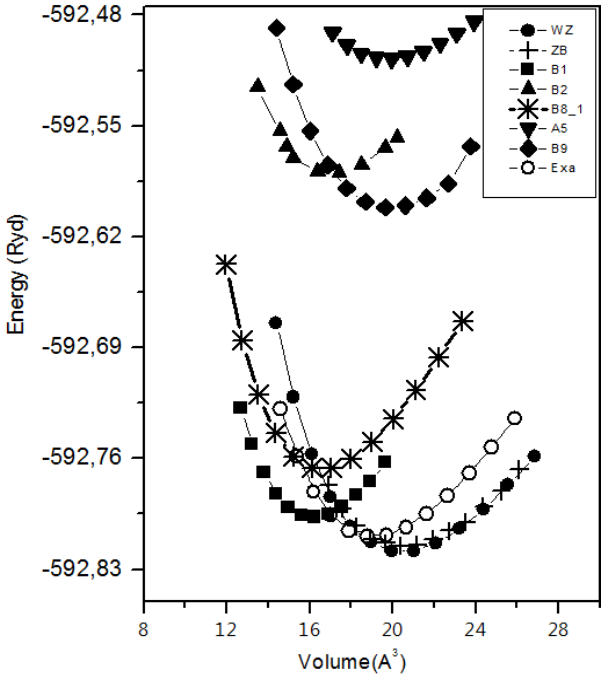

Fig. 1 **.** Computed total energy versus unit-cell volume for the phases structures of AlN compound.

phase	V_0	*a*	*b/a*	*c/a*	*u*	*B'*	$B_\circ$
WZ	*40.866**	3.0922	1.000	1.595	0.382	3.7	198.006
		3.10[a]	1.0000	1.6[a,t]	0.3823[a]	3.87[a]	207.84[a]
		3.093[b]		1.601[b]	0.3801[b]	3.7[t]	212.16[b]
		3.084[c]		1.604[c]	0.3814[c]	3.878[b]	205[e,i]
		3.111[f]		1.601[f]	0.385[f]	5.7-6.3[f]	185-212[f]
ZB	*20.45**	*4.34*	*1.000*	*1.000*		*3.766*	197.271
		4.36[a]				3.95[a]	208.27[a]
		4.349[b]				3.90[b]	211.78[b]
		4.302[t]				3.7[t]	210[t]
NaCl	16.18*	4.016	1.000	1.000		4.12	268.471
		4.03[a]				4.02[a]	274.87[a]
		4.014[b]				3.99[b] 3.8[t]	276.6[b]
		3.978[t]					272[t]
		4.045[w]				4.02[w]	274.87[w]
Hexa	19.059*	3.29	1.000	1.23	0.5	3.902	214.1887
NiAs	33.13*	2.830	1.000	1.688	0.25	3.896	249.347
				1.72[i]	0.25[i]		

Table 1: Calculated structural parameters equilibrium volumes V_0 (in $Å^3$), lattice constants a, (in Å), structural parameter c/a, b/a, and the internal structural u and (*v*for B9 phase), and bulk moduli B_0 (in GPa) and their first derivatives B', for different phases analyzed for AlN compound. With: * present work, a: Ref. [13] , b: Ref. [14], c: Ref. [15], f: Ref. [16-19], t: Ref. [7], g: From wurtzite structure Ref. [20], w: Ref. [21]. i: Ref. [12].

3.2. Phase transition

To determine the most stable structure at finite pressure and temperature, we have compared the enthalpies $H=E+PV$ of the different phases instead of their free energies $G=E+PV-TS$ since we consider the temperature constant. The calculated transition pressures (P_T) are given in Table 2.

The most stable structure obtained is the wurtzite one. The zinc-blende, hexagonal, rock-salt and NiAs structures are the high pressure phases and the zinc-blende structure is more stable than that of rock-salt. The present FPLMTO result for the transition pressure from the wurtzite to the rock-salt structure is of 13.5GPa, which is closed to those reported in Ref. [22], and Ref. [12].

We calculated a transition pressure of AlN from zinc-blende to rock-salt structure at P_T = 8 GPa. This result agree very well with the calculated value of 7.1 GPa in Ref. [7] .We also report that for AlN a transition pressure from zinc-blende to Hexa occurs at 15 GPa,and from Hexa to rocksalt at 10.5 GPa. However, no theoretical values and experimental data have been reported so far regarding these transitions. We predict a transition pressure of AlN from wurtzite to zinc blende at P_T = 8.2 GPa, and from wurtzite to hexagonal structure at P_T = 18.5 GPa Likewise, no theoretical values and experimental data have been reported so far, to the best of our knowledge regarding these transitions.

The case of transition pressure from rock-salt to NiAs is of particular interest because in Ref.12, authors have theoretically predicted a value of 30-35 GPa. However a recent experiment study in Ref. 23 didn't find any evidence of $B8_1$structure up to very high pressure of 132 Gpa. This is in agreement with our calculation when we find in this case a transition of 215Gpa. We note that in the present study of AlN, the CsCl (B2), the βSn (A5) and the Cinnabar (B9) structures are not close to stability in any range of pressures of interest.

Phase	P_T(GPa)	Volume
B4 to Hexa	18.5	$V_{(B4)}$: 37.72 $V_{(Hex)}$:17.69
B3 to Hexa	15	$V_{(B3)}$: 19.13 $V_{(Hex)}$: 17.91
Hexa to B1	10.5	$V_{(Hex)}$: 18.22 $V_{(B1)}$: 15.62
B4 to B1	13.5 12.9[u] 14-16.6[w]	$V_{(B4)}$: 38.46 $V_{(B1)}$: 15.46
B3 to B1	8 7.1[t]-5[y]	$V_{(B3)}$:19.70 $V_{(B1)}$:15.73
B4 to B3	8.2	$V_{(B4)}$: 39.32 $V_{(B3)}$:19.68

Table 2: Transition pressures P_T(GPa) for AlN, with: t: Ref. [7], u: Ref. [22], w: Ref. [21], y: Ref. [24].

4. Conclusion

We have carried out first-principles band structure and total-energy calculations of AlN for B1, B2, B3, B4, B8-1, A5, B9 and the hexagonal structures within the framework of the local density approximation (LDA). We have used a recent version of the full potential linear muffin-tin orbitals method (FPLMTO) augmented by a plane-wave basis (PLW) as implemented in the lmtART code. We confirm that the wurtzite structure is the most stable at ambient pressure. We found that AlN will transform from B4 to B3 phase structure at 8.2 GPa. And from B3 to B2 structure at 8 GPa. This is a consistent with the results found from the literature. In the absence of experimental findings and support regarding the transition pressure from B4 and B3 to hexagonal structures for AlN, our results may serve as a reference. Our result from B2 to NiAs transition is in good agreement with experimental values.

Acknowledgements

The authors thank S.Y.Savrasov for his Mindlab software freely available. One of the authors thanks Pr.N.Sekkal for his help and advice .This work has been supported by the Algerian national research projects CNEPRU D05520060007 and E05520070007.

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